

## AMINOSULPHINYL CHLORIDES—THEIR PREPARATION, AND REACTIONS WITH THE Si–NBOND

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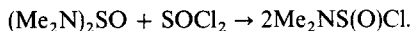
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**Abstract**—The reactions of aminosulphinyl chlorides, prepared best from the appropriate aminosilane and thionyl chloride, with silicon–nitrogen compounds are examined, and compared with similar reactions of aminosulphenyl chlorides.

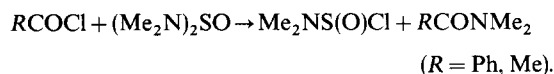
### INTRODUCTION

AMINOSULPHINYL chlorides have been synthesized directly from secondary amines and thionyl chloride [1a], from bis(dimethylamino)sulphoxide and dipropylboron chloride [1b] or aminosulphinates and thionyl chloride [1c]. However, the direct method was found to lead to violent decomposition. Consequently other more convenient routes have been investigated, following in some cases those employed for aminosulphenyl chlorides [2]. The reaction of bis(dimethylamino)sulphoxide with thionyl chloride gave a good yield of pale yellow, hygroscopic dimethylaminosulphinyl chloride.



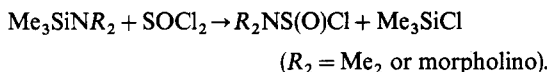
This mildly exothermic reaction was also found to be a convenient synthesis for morpholinosulphinyl chloride, but the attempted preparation of diethylaminosulphinyl chloride, or higher aliphatic homologues, from the sulphoxide led to extensive decomposition which may be explosive above 80°.

Bis(dimethylamino)sulphoxide was found to react exothermically with both benzoyl and acetyl chloride. A good yield of the aminosulphinyl chloride resulted with the former but was poor for acetyl chloride.



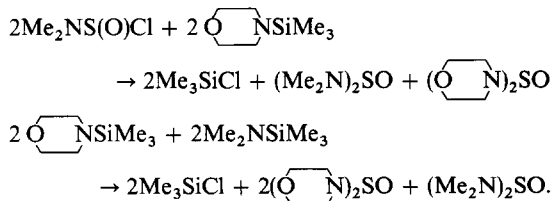
The most convenient synthetic method is probably the equimolar reaction of thionyl chloride and the appropriate aminosilane. This strongly exothermic reaction has already been used to prepare bisaminosulphoxides [3]. However, as with the synthesis from

bisaminosulphoxides and thionyl chloride,



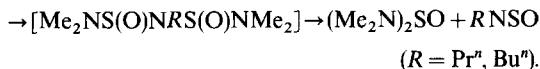
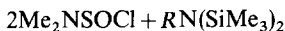
diethylaminosulphinyl chloride decomposed on distillation.

Apart from the reactions of aminosulphinyl chlorides with amines, to give symmetrical sulphoxides [1c] these compounds seem to have been little studied. As with the reactions of aminosulphenyl chlorides with aminosilanes [2], the attempted preparation of unsymmetrical bisaminosulphoxides was unsuccessful. Thus dimethylaminosulphinyl chloride reacts very exothermically with morpholinotrimethylsilane in diethyl ether at –78° but only the two symmetrical aminosulphoxides could be isolated. A similar situation occurred with morpholinosulphinyl chloride and dimethylaminotrimethylsilane.

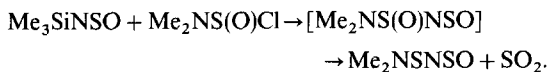


Aminosulphenyl chlorides yield triazadithianes with disilazanes [2]. With similar chlorides of tetravalent sulphur, however, the triazasulphoxide is not stable, forming instead, the bisaminosulphoxide and *n*-alkylsulphinylamine. Thus with dimethylaminosulphinyl chloride and *N*-substituted hexamethyldisilazanes (substituent is  $\text{Pr}^n$  or  $\text{Bu}^n$ ), the sulphinylamines were formed,

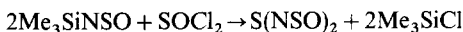
due, possibly to the added stability of the sulphur-nitrogen double bond.



Sulphinylaminodialkaminosulphides (dialkylcatena(azathian)-3-ene 4-oxide),  $\text{R}_2\text{NSNSO}$ , result from sulphinylaminotrimethylsilane and the sulphenyl chloride[2]. The methyl homologue is formed, albeit in poor yield, along with  $\text{SO}_2$ , from the reaction of the sulphinylaminosilane  $\text{Me}_3\text{SiNSO}$  and dimethylaminosulphinyl chloride.



Likewise, attempts to prepare bis(sulphinylamino)sulphoxide,  $\text{OS}(\text{NSO})_2$ , from thionyl chloride and sulphinylaminotrimethylsilane gave only the chlorosilane and bis(sulphinylamino)sulphide as characterizable products.



The latter results in excellent yield using sulphur dichloride[4].

This tendency to produce mixed valency states in polythio compounds from compounds of S(IV) is being further investigated.

## EXPERIMENTAL

All compounds were handled under anhydrous conditions and, where necessary, reactants were cooled before addition. Bis(dimethylamino)sulphoxide was prepared by adding thionyl chloride to an excess of dimethylamine in diethyl ether as solvent[1b, 5]. The aminosilanes and disilazanes were prepared from trimethylchlorosilane and the appropriate amine by reported methods[6].

### *Interaction of bis(dimethylamino)sulphoxide with thionyl chloride*

The thionyl chloride (7.2 g, 1.0 mole) was slowly added to the aminosulphoxide (8.8 g, 1.0 mole) with cooling as the reaction was very exothermic. Vacuum distillation of the liquid so formed gave pale yellow fuming dimethylaminosulphinyl chloride (8.3 g, 52%), b.p.  $60^\circ/3$  mm,  $n_D^{25}$  1.5307 (Found: C, 19.0; H, 4.6; N, 10.8; S, 25.3; Cl, 28.2. Calc. for  $\text{C}_2\text{H}_6\text{NSOCl}$ : C, 18.8; H, 4.7; N, 11.0; S, 25.1; Cl, 27.8%). The i.r. spectrum show strong absorptions at 1190, 950 and  $700\text{ cm}^{-1}$ , ascribed to  $\nu_{\text{S}=\text{O}}$ ,  $\nu_{\text{S}}(\text{NC}_2)$  and  $\nu_{\text{S}-\text{N}}$ , along with a single peak in the PMR spectrum at  $\tau$  7.13.

### *Interaction of bis(dimethylamino)sulphoxide with benzoyl chloride*

Benzoyl chloride (8.1 g, 1.0 mole) was added to the sulphoxide (7.8 g, 1.0 mole) in diethyl ether (30  $\text{cm}^3$ ) at room temperature. The solution warmed on addition, and went deep yellow. After separating the solvent at 1 mm vacuum, distillation gave dimethylaminosulphinyl chloride (4.3 g, 58%), b.p.  $44^\circ/0.2$  mm,  $n_D^{24}$  1.5300 and N,N-dimethylbenzamide (2.1 g, 25%), b.p.  $75\text{--}80^\circ/0.25$  mm.

A similar reaction between acetyl chloride and the

sulphoxide yielded a mixture of N,N-dimethylacetamide (0.7 g, 14%), b.p.  $31^\circ/3.5$  mm,  $n_D^{20}$  1.4394 and dimethylaminosulphinyl chloride (0.4 g, 5%), b.p.  $60^\circ/4$  mm,  $n_D^{20}$  1.5280, separated using a spinning band column.

### *Interaction of dimethylaminotrimethylsilane and thionyl chloride*

Thionyl chloride (6.8 g, 1.0 mole) was slowly added to the aminosilane (6.7 g, 1.0 mole) in ether (30  $\text{cm}^3$ ) at  $-78^\circ$ . The vigorous reaction gave a yellow liquid and the ether and chlorosilane were pumped into a trap. This mixture yielded chlorotrimethylsilane (5.1 g, 85%), b.p.  $57^\circ$ ,  $n_D^{25}$  1.3860. The yellow residue was vacuum distilled giving dimethylaminosulphinyl chloride (5.3 g, 73%), b.p.  $50^\circ/0.2$  mm,  $n_D^{25}$  1.5300.

### *Interaction of morpholinotrimethylsilane and thionyl chloride*

The thionyl chloride (5.5 g, 1.0 mole) was added to the silane (7.4 g, 1.0 mole) in diethyl ether (30  $\text{cm}^3$ ) at  $-78^\circ$ , as the reaction was vigorous. The ether and trimethylchlorosilane were pumped off at room temperature and separated by distillation, giving the latter (3.6 g, 72%) as a colourless liquid, b.p.  $57^\circ$ ,  $n_D^{25}$  1.3864. Vacuum distillation of the residue gave morpholinosulphinyl chloride as a yellow liquid (5.1 g, 67%), b.p.  $63^\circ/0.02$  mm,  $n_D^{25}$  1.5761 (Found: C, 27.1; H, 4.3; N, 8.4. Calc. for  $\text{C}_4\text{H}_8\text{NSO}_2\text{Cl}$ : C, 27.3; H, 4.7; N, 8.3%).

### *Interaction of morpholinosulphinyl chloride with dimethylaminotrimethylsilane*

The chloride (7.6 g, 1.0 mole) was added to the silane (5.2 g, 1.0 mole) in ether (30  $\text{cm}^3$ ) at  $-78^\circ$ . The reaction was vigorous and subsequent warming gave ether and trimethylchlorosilane (2.9 g, 60%), b.p.  $57^\circ$ ,  $n_D^{25}$  1.3860 as a trapped residue along with bis(dimethylamino)sulphoxide (1.2 g, 39%), b.p.  $52^\circ/4$  mm, m.p.  $34^\circ$  possessing a singlet in the PMR spectrum at  $\tau$  = 7.45. The residue was recrystallized from ether to yield bismorpholinosulphoxide (2.3 g, 48%) as white crystals, m.p.  $90^\circ$ .

Dimethylaminosulphinyl chloride and morpholinotrimethylsilane reacted similarly giving trimethylchlorosilane (5.6 g, 77%), b.p.  $57^\circ$ ,  $n_D^{25}$  1.3863, bis(dimethylamino)sulphoxide (2.0 g, 45%), b.p.  $52^\circ/4$  mm, m.p.  $34^\circ$  and bismorpholinosulphoxide (3.4 g, 47%), m.p.  $90^\circ$ .

### *Interaction of dimethylaminosulphinyl chloride with N-n-propylhexamethyldisilazane*

The addition of the sulphinyl chloride (11.5 g, 2.0 mole) to the silazane (9.2 g, 1.0 mole) in diethylether (30  $\text{cm}^3$ ) was exothermic, so was cooled in an ice-bath and stirred. Volatile products were pumped off at 10 mm, trapped and fractionated giving ether and trimethylchlorosilane (8.4 g, 86%), b.p.  $56^\circ$ ,  $n_D^{25}$  1.3865 along with N-sulphinyl-n-propylamine (1.7 g, 36%), b.p.  $28^\circ/50$  mm,  $n_D^{25}$  1.4310 (Found: C, 34.2; H, 6.76; N, 13.2; S, 30.3. Calc. for  $\text{C}_3\text{H}_7\text{NSO}$ : C, 34.3; H, 6.65; N, 13.3; S, 30.5%). The residue yielded bis(dimethylamino)sulphoxide (5.2 g, 84%), b.p.  $54^\circ/4$  mm, m.p.  $32^\circ$ .

N-Sulphinyl-n-butylamine (70%), b.p.  $34^\circ/14$  mm,  $n_D^{21}$  1.4384 (b.p.  $50^\circ/36$  mm,  $n_D^{20}$  1.4367)[3] was prepared similarly.

### *Interaction of dimethylaminosulphinyl chloride and sulphinylaminotrimethylsilane*

The sulphinyl chloride (9.2 g, 1 mole) was slowly added to the silane (9.7 g, 1 mole) with stirring. The colour darkened to deep red, and gentle heating resulted in the evolution of  $\text{SO}_2$ , detected using dichromate and litmus. The chlorosilane formed was trapped and purified (4.6 g, 59%), b.p.  $57^\circ$ ,

$n_D^{25}$  1.3869. Vacuum distillation of the residue yielded dimethylamino(sulphinylamino)-sulphide as a yellow liquid (2.1 g, 21%), b.p. 39°/7 mm,  $n_D^{25}$  1.5405 (Found: C, 18.2; H, 4.81; N, 20.3; S, 46.8. Calc. for  $C_2H_6N_2S_2O$ : C, 17.4; H, 4.35; N, 20.3; S, 46.4%).

*Interaction of dimethylaminotrimethylsilane and thionyl silane*

Thionyl chloride (4.8 g, 1 mole) was added to the sulphinylamine (11.2 g, 2 mole). There appeared to be no heat of mixing so the mixture was heated under reflux for 2 days, when, on cooling, golden platelets were formed. The volatile constituents were removed and trapped, fractionation giving trimethylchlorosilane (4.9 g, 57%), b.p. 57°,  $n_D^{25}$  1.3868. Recrystallization of the platelets from trimethylchlorosilane

yielded crystals of bis(sulphinylamino)sulphide (3.1 g, 42%), m.p. 100°[4].

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